Nanoscopic Metal Oxide Objects *via* Controlled Creation and Rearrangement of Amorphous Nanoparticles

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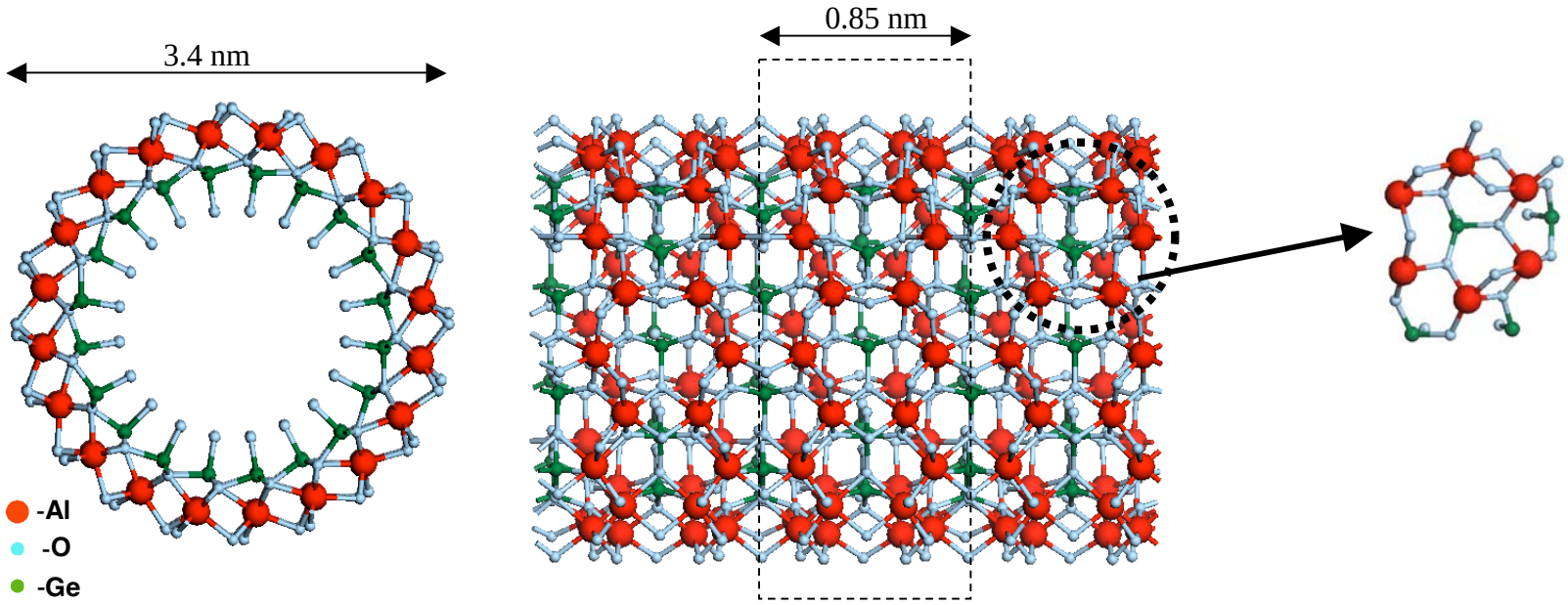
Assembly of Nanoscopic Metal Oxide Objects

- Metal oxides offer a vast range of technologically interesting properties …. catalytic, transport, mechanical, electronic, optical
- Shrinking them into nanoscopic objects (nanotubes, nanoshells) offers exciting prospects for new nanotechnological materials and nanoscale devices
- Metal oxide assembly in aqueous phase can be controlled by a variety of handles – temperature, pH, electrolytes
- Can single-walled metal oxide nanotube objects be assembled from precursors ?
- Can the shape, size, curvature, composition be controlled ?
- What are the chemical/physical limits of such engineering ?
- Existence of a unique model system to study these issues: precursor to a possible generalized strategy for metal oxide nanotube engineering ?

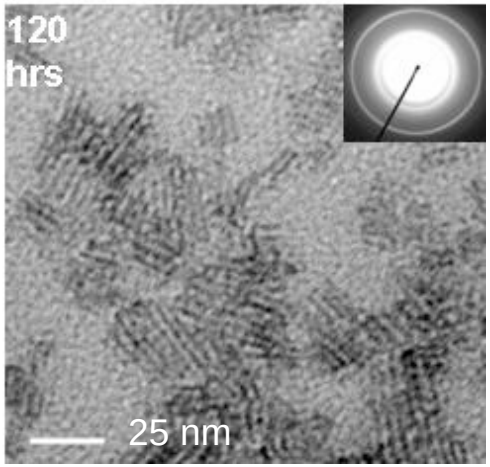
Aluminogermanate (Al-Ge) Nanotubes

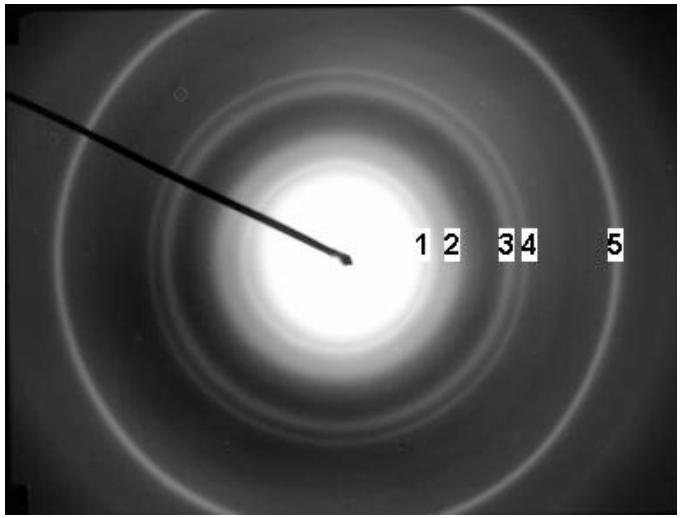


- Hydrophilic aluminum hydroxide shell
- Pendant germanol groups
- Exclusively single walled nanotubes with precise outer and inner diameters
- Average length ~ 20 nm*

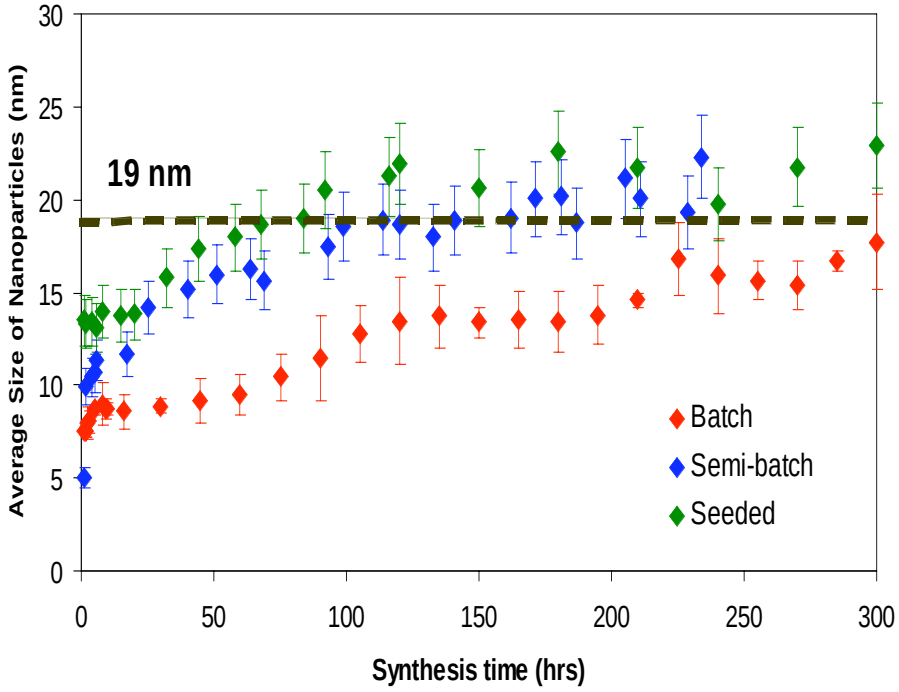
* Mukherjee et. al, *Chemistry of Materials* (2005)

Aluminogermanate (Al-Ge) Nanotubes





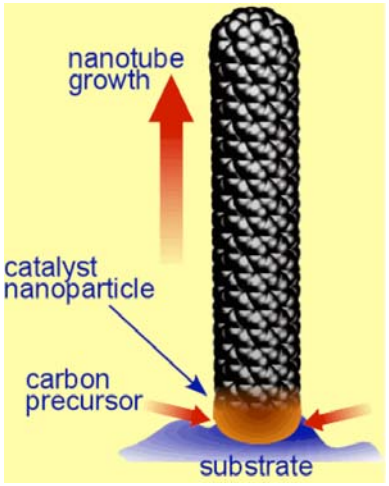
- Ordered single-walled nanotube materials by aqueous-phase synthesis
- Early evidence of non-conventional growth mechanism



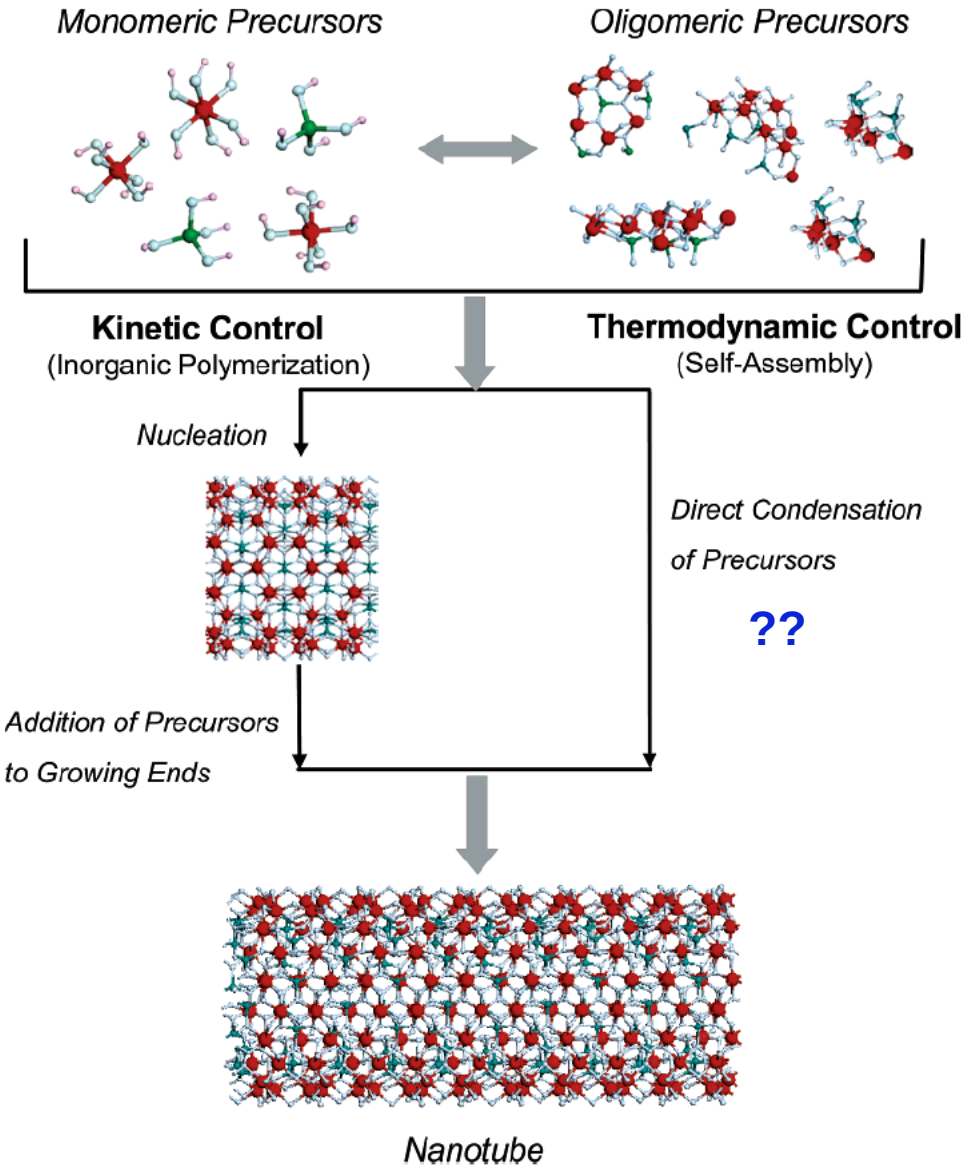
Mukherjee et. al, *Chemistry of Materials* (2005)

Mukherjee et al, *Journal of the American Chemical Society* (2007)

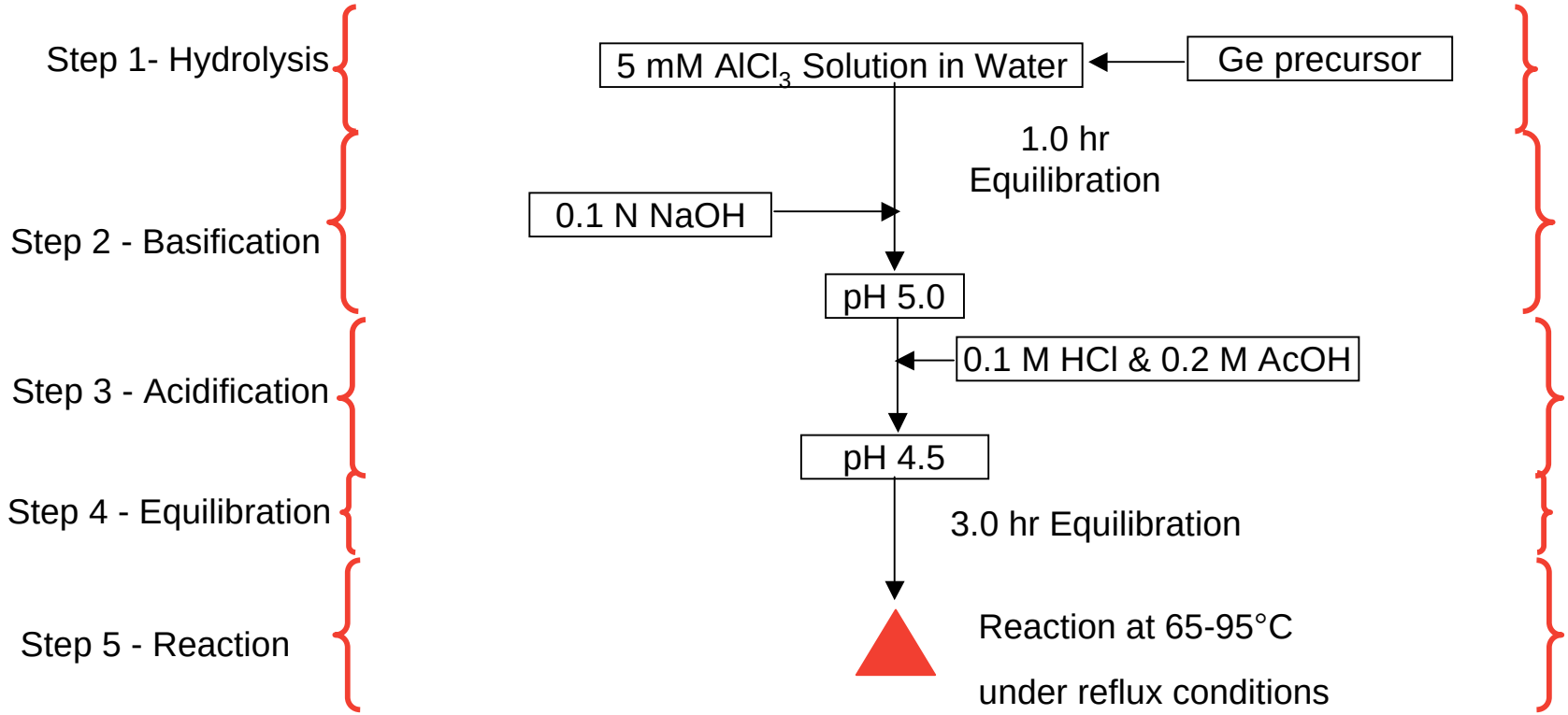
Nanotube Growth Mechanisms



http://homepages.ed.ac.uk



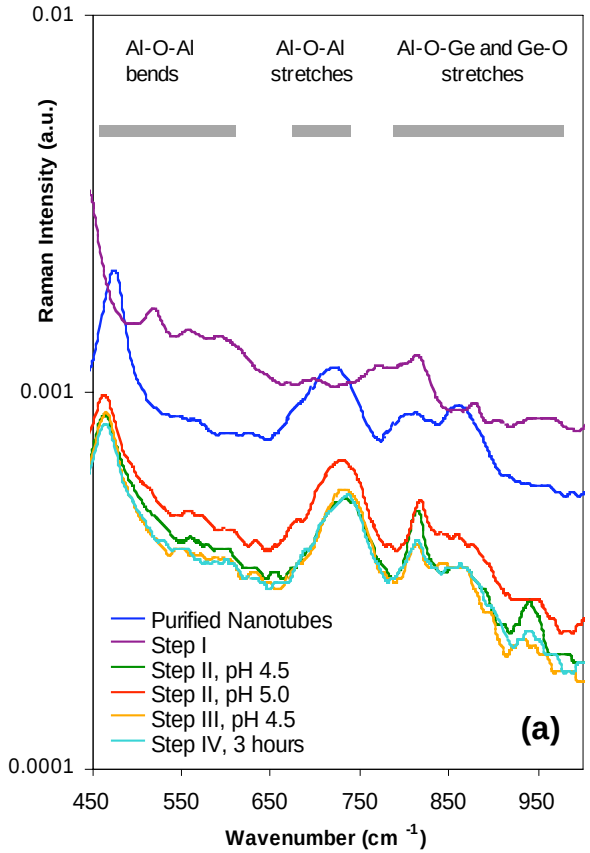
Aluminogermanate Nanotube Synthesis Process

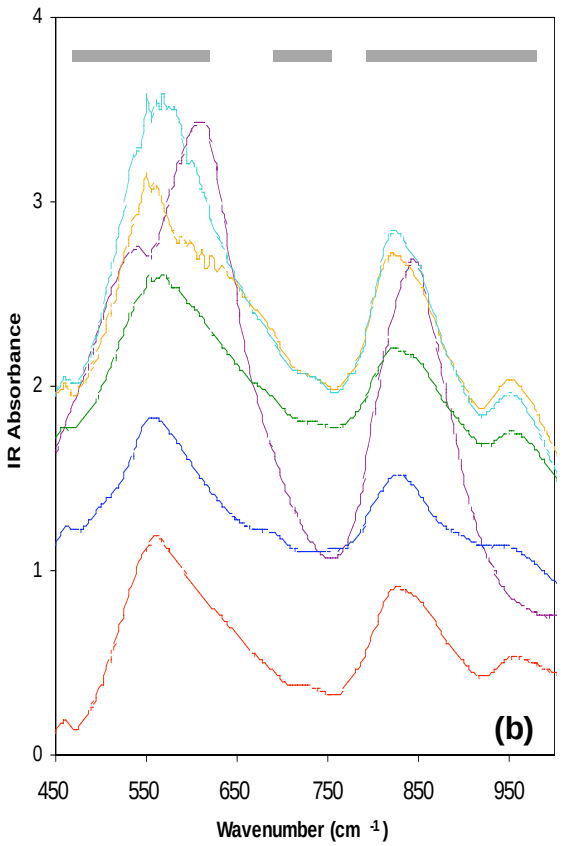


- Importance of Steps 1-4
  - Chemical environment of synthesis solution
  - Characterization of evolving colloid at each step

Chemical Environment of Precursors in Steps 1-4

FT-Raman



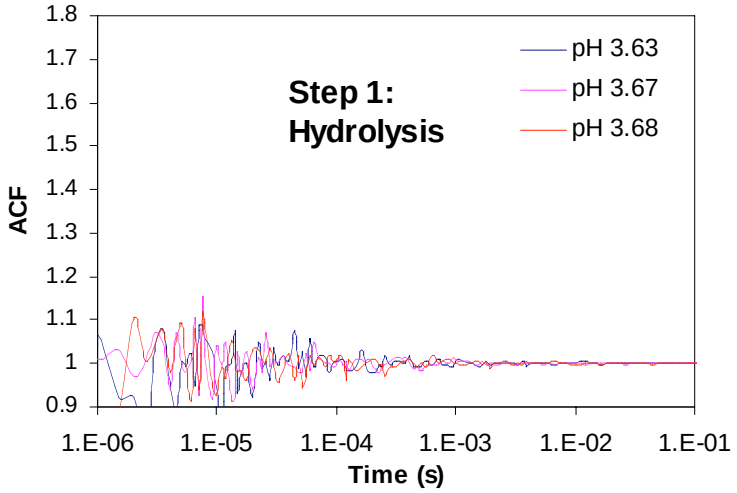


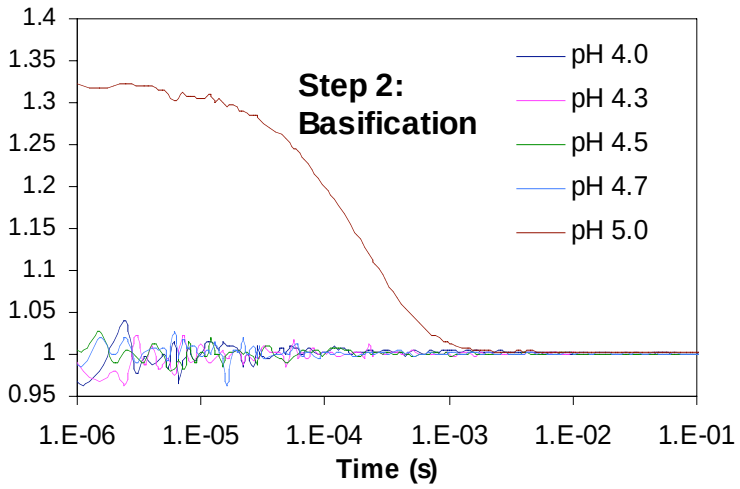
FT-IR

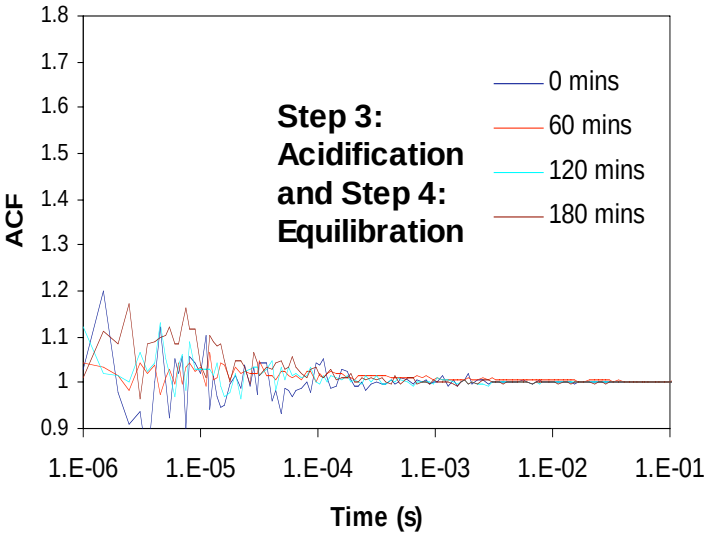
- Step 1 (hydrolysis) product is significantly different from all other products
- Chemically, the products of Step 2, 3 & 4 are similar to that of the final nanotube i.e., Al-O-Ge bonds have been established

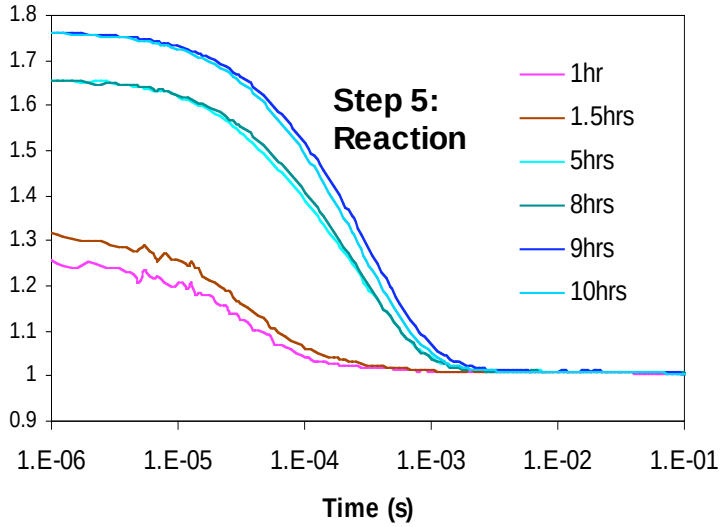
Mukherjee et al, *Journal of the American Chemical Society* (2007)

Nanoparticle Evolution - Dynamic Light Scattering



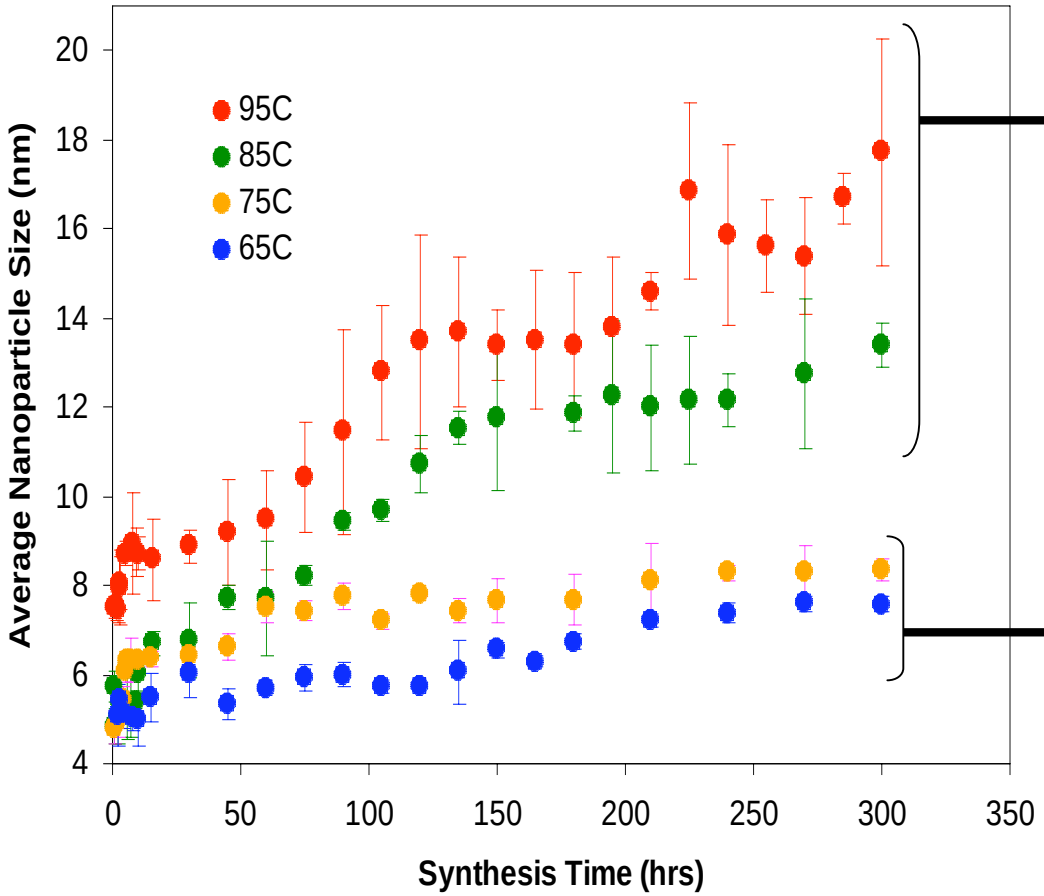






- pH control (basification) condenses precursors to form oligomers with Al-O-Ge bonds
- Re-acidification prevents precipitation of amorphous materials

Average Nanoparticle Size from DLS

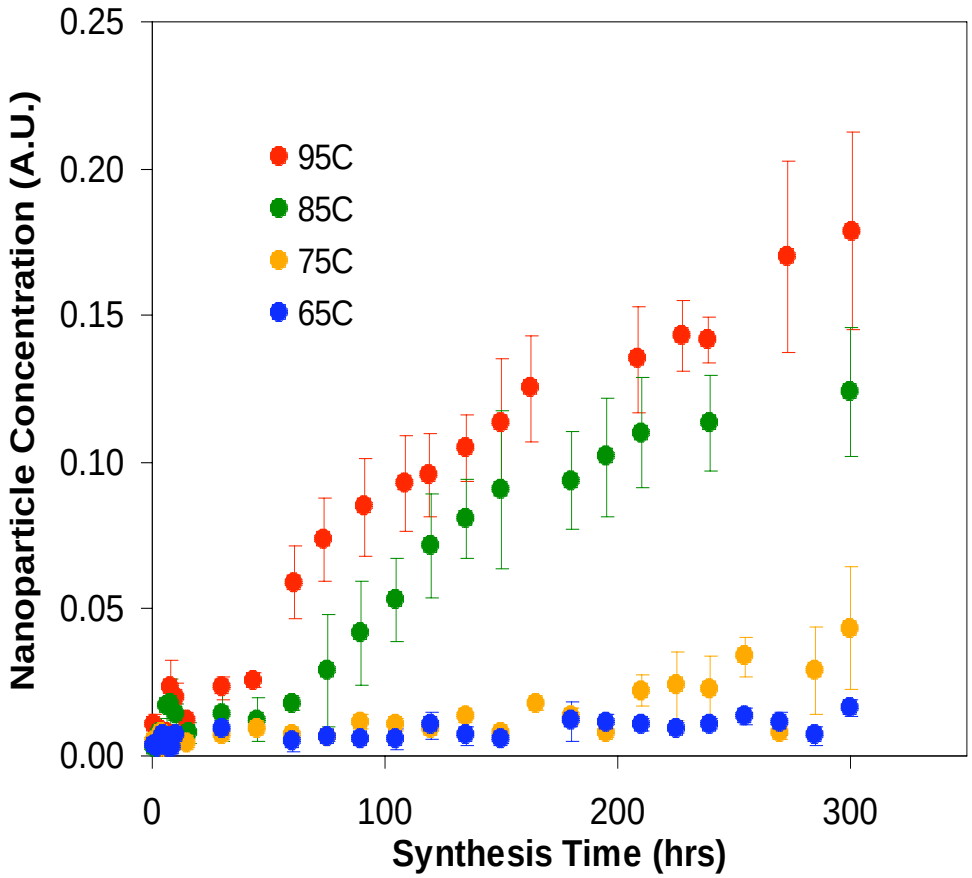


Nanotubes present

Nanotubes not detected with TEM, ED, or XRD characterization

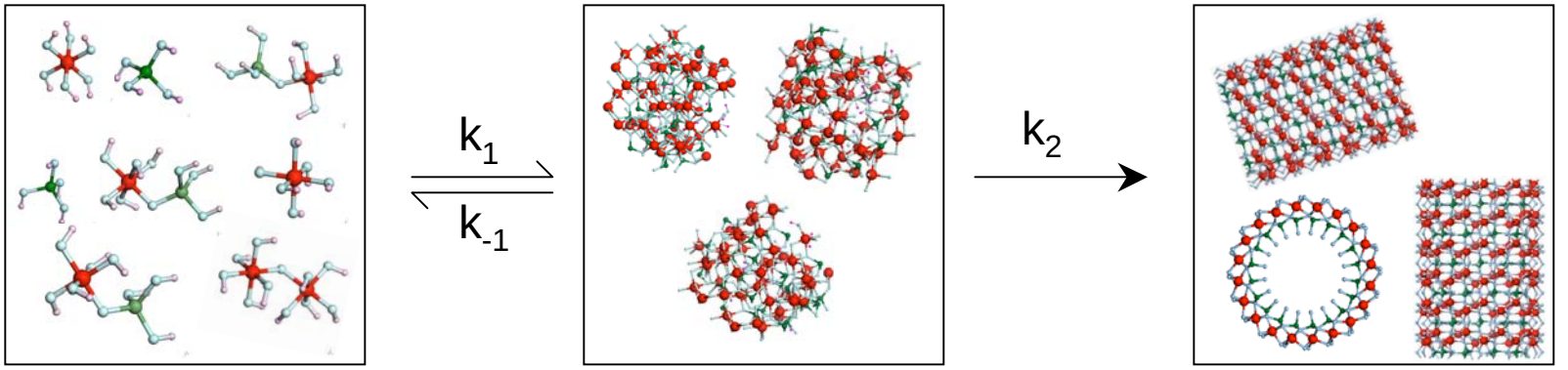
- At 95°C and 85°C average nanoparticle size increases slowly
- Even though no nanotubes are detected in 65°C and 75°C, nanoparticles are present

Concentration of Nanoparticles – DLS Intensity



- DLS intensity normalized by particle size is a measure of concentration
- Nanoparticle concentration increases by almost two orders of magnitude when nanotubes are formed

Mechanism of Al-Ge Nanotube Assembly



Precursors (P) Amorphous Nanoparticles (ANP) Ordered Nanotubes (NT)

- The precursors first condense into Amorphous NanoParticles (ANPs)
- The ANPs rearrange into ordered NanoTubes (NTs)
- A simple model was developed that assumes:
  - A quasi steady-state for the amorphous nanoparticles ($dC_{ANP}/dt \sim 0$)
  - The concentrations of nanotubes changes, dimensions remain constant

Mukherjee et al, *Journal of the American Chemical Society* (2007)

Quantitative Kinetic Model - Solution

C_{NT} = Concentration of nanotube C_{ANP} = Concentration of amorphous nanoparticles

$$\frac{dC_P}{dt} = -k_1 C_P + k_{-1} C_{ANP}$$

$$\frac{dC_{ANP}}{dt} = \frac{k_1 C_P}{N_P} - \frac{k_{-1} C_{ANP}}{N_P} - k_2 C_{ANP} = 0 \quad (QSS)$$

$$\frac{dC_{NT}}{dt} = k_2 C_{ANP}$$

$$C_P(t) = C_{P_0} e^{-Kt}$$

$$K = \frac{k_1 k_2}{\frac{k_{-1}}{N_p} + k_2}$$

Overall effective NT formation rate constant

$$C_{ANP}(t) = \frac{C_{P_0} K}{k_2 N_P} e^{-Kt}$$

$$C_{NT}(t) = \frac{C_{P_0}}{N_P}\left[1 - e^{-Kt}\right]$$

Fitting Model Parameters with Experimental Data

Average particle size in DLS is due to both ANPs and NTs

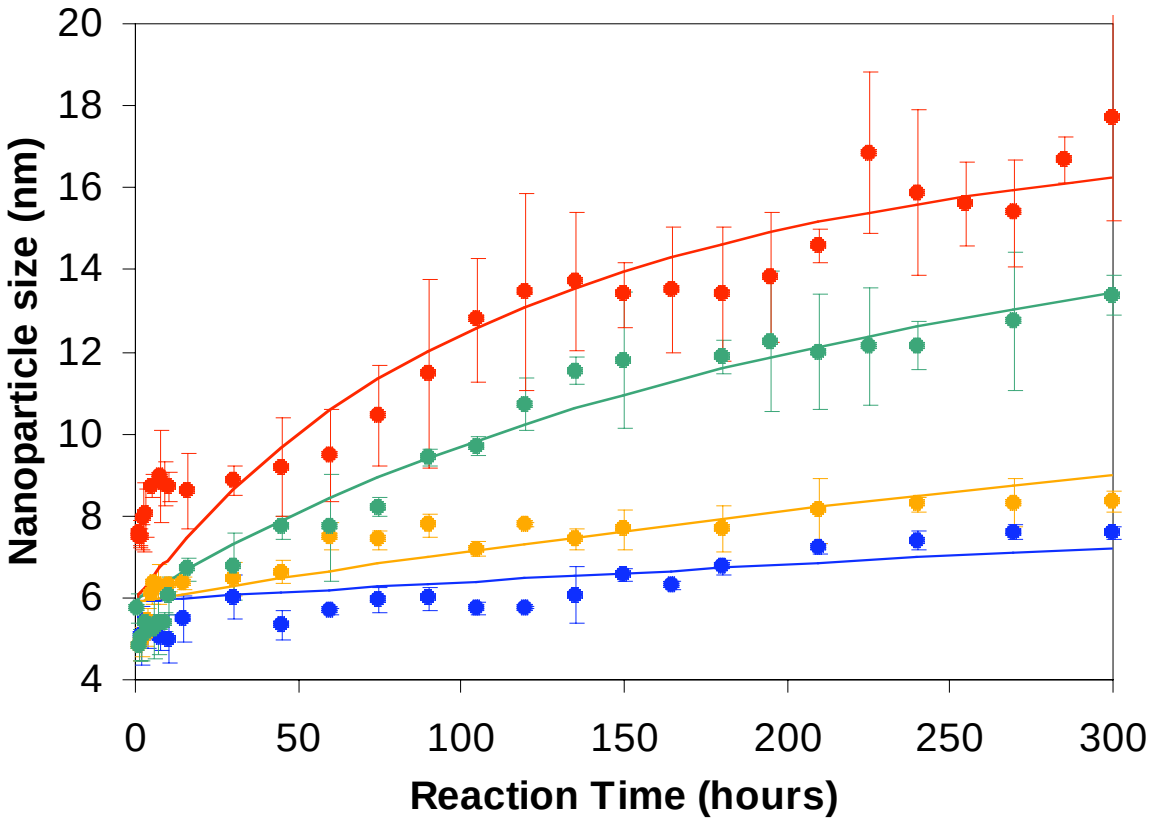
$$L_{DLS} = \frac{L_{ANP}C_{ANP} + L_{NT}C_{NT}}{C_{ANP} + C_{NT}}$$

$$L_{ANP} = 5.9 \quad nm$$

$$L_{NT} = 17.6 \quad nm$$

$$C_{ANP}(t) = \frac{C_{P_0}K}{k_2 N_P} e^{-Kt}$$

$$C_{NT}(t) = \frac{C_{P_0}}{N_P}\left[1 - e^{-Kt}\right]$$



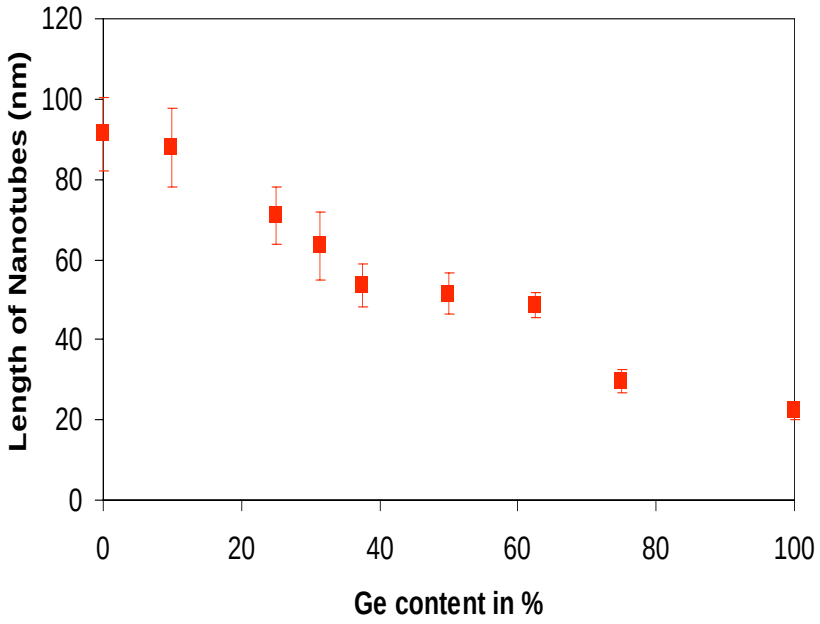
- Increase in average particle size is due to the ANP → NT transformation

Effects of Composition (Si/Ge ratio)

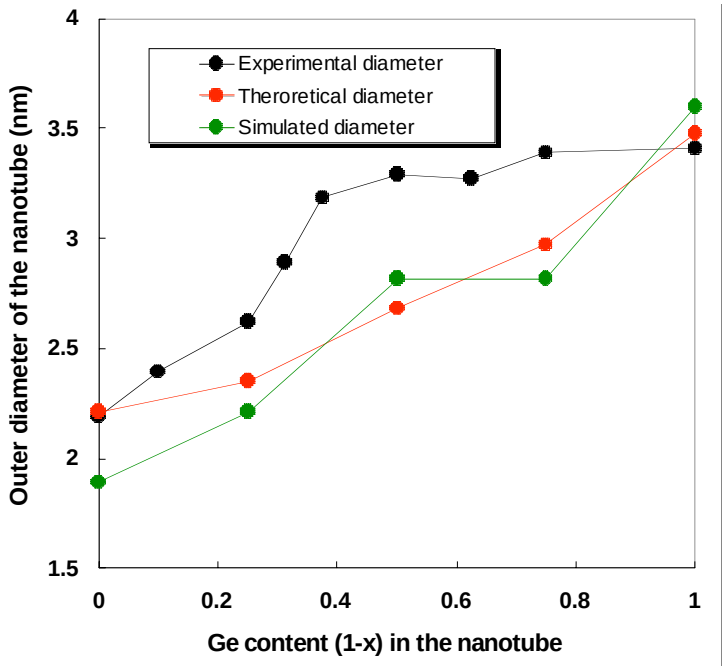
Progressive substitution of Ge with Si allows a series of Al-Ge-Si nanotubes

What is the effect of Si/Ge ratio on the mechanism of AlSiGe nanotube formation in the framework of the ANP → NT mechanism ?

Length Control



Diameter Control

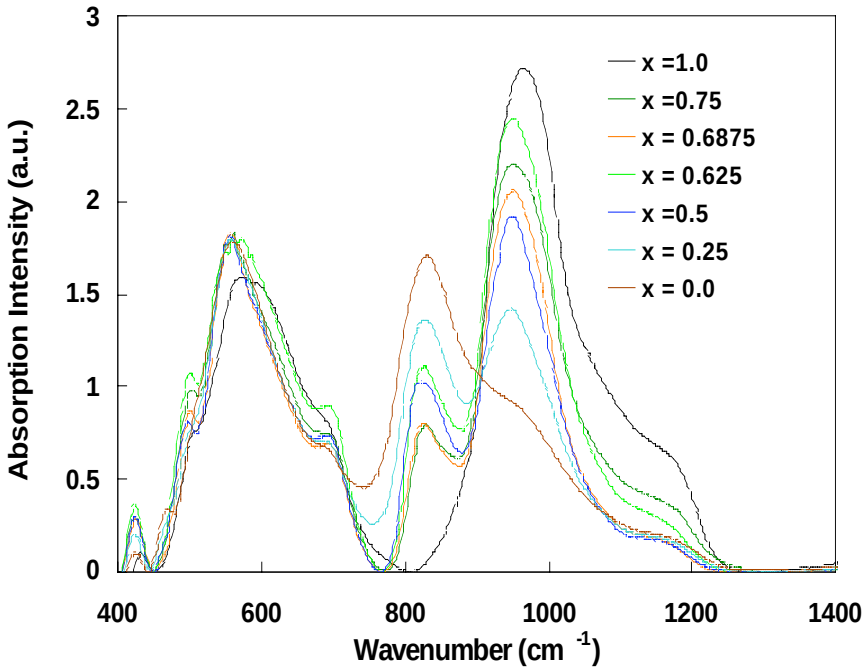


- Length increases from ~20 nm in Al-Ge to ~100 nm in Al-Si nanotubes

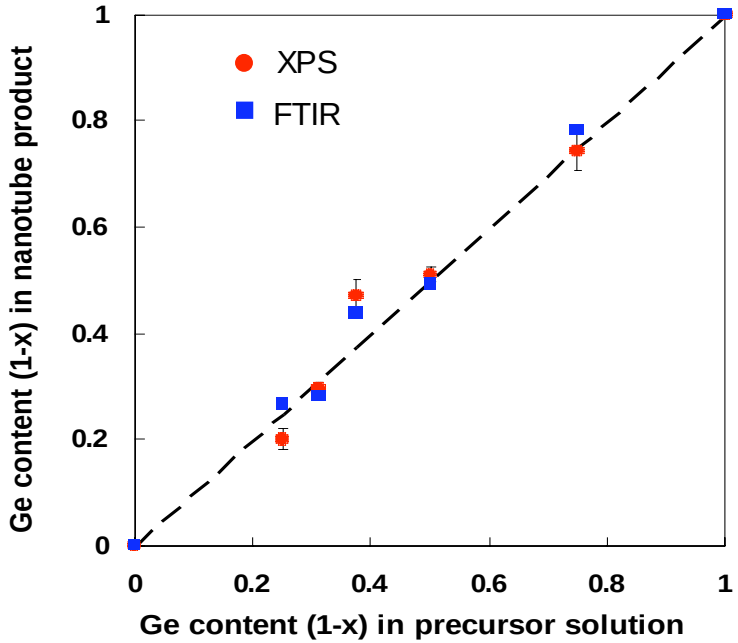
- Diameter decreases from 3.4 nm in Al-Ge to 2.2 nm in Al-Si nanotubes

Composition of Nanotubes - XPS and FTIR Analysis

FTIR spectra of freeze dried NTs

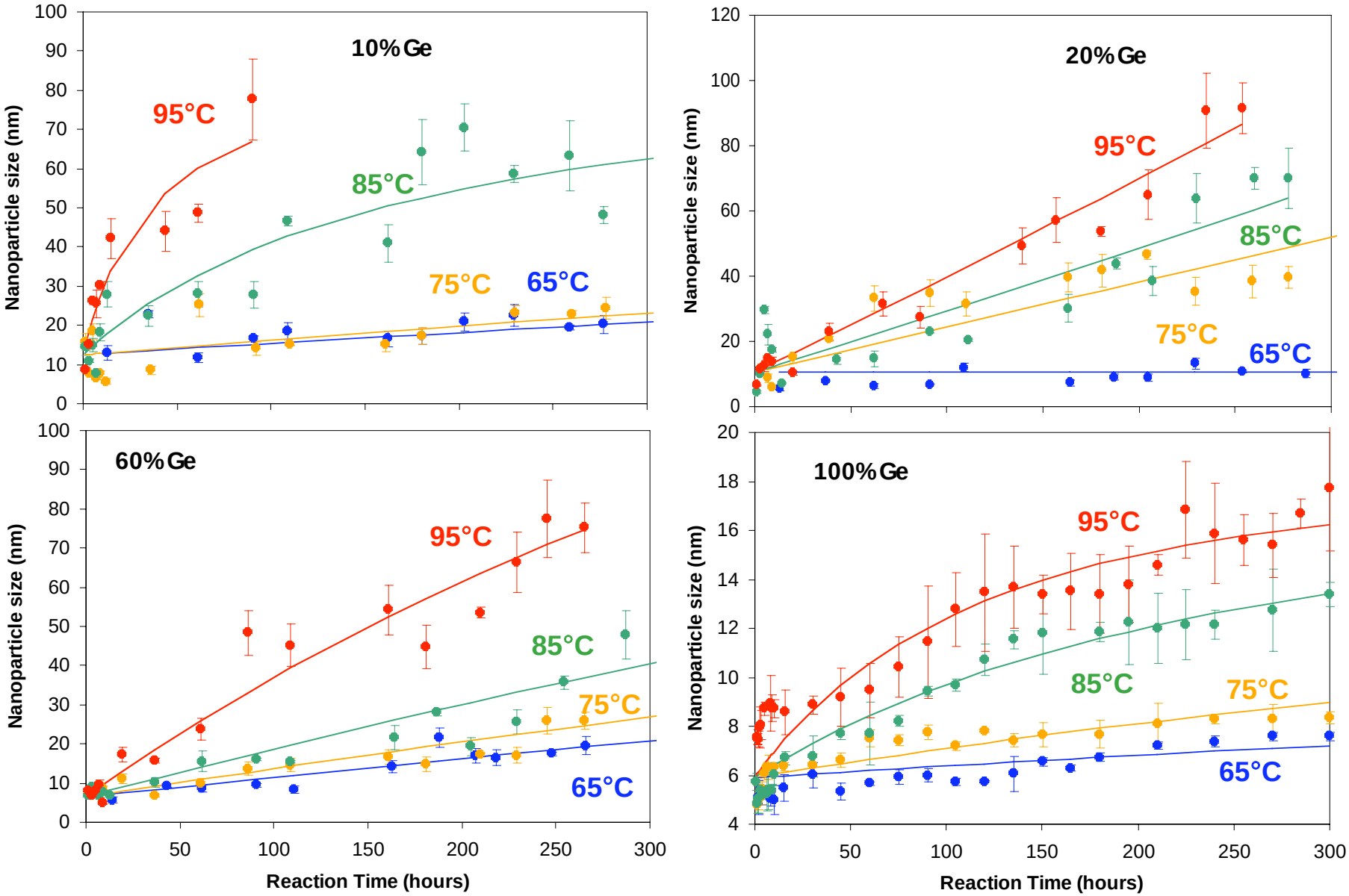


NT composition analysis by FTIR and XPS



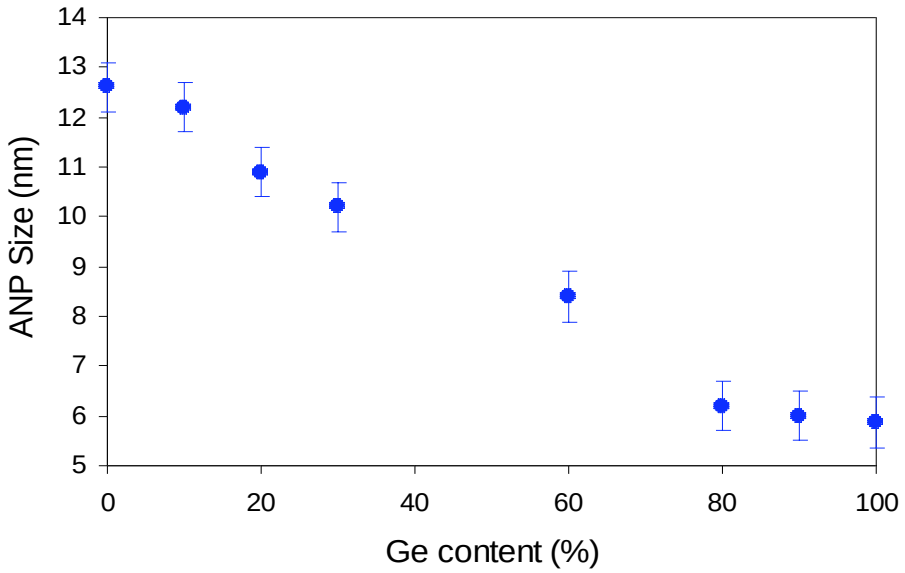
- Ge content in the final product follows closely the precursor composition
- Ge content can be reproducibly varied and measured

Dynamic Light Scattering Investigations

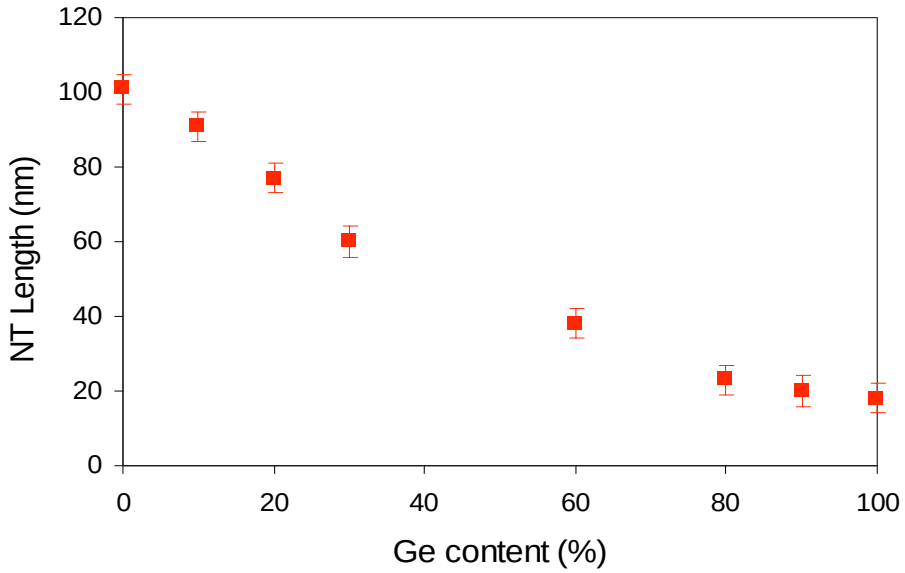


ANP and NT Sizes Extracted from DLS Data

Fitted ANP Size



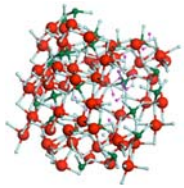
Fitted NT Length



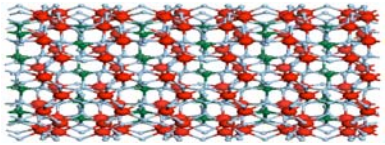
- The Amorphous Nanoparticle size is dependent on the Si/Ge ratio
- Both ANPs and NTs show the same trend of decreasing size as Ge content increases

Extrapolation of ANP Size from NT Length

AlGe Nanotube



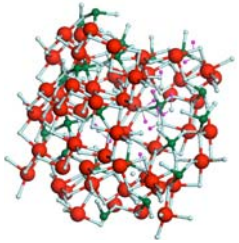
5.87 nm



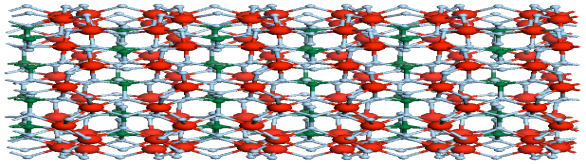
17.6 nm

14.3 Al atoms/nm^3

Al-Si-Ge Nanotube with 10% Ge



x nm



91 nm

→ **x = 10.1 nm**

- These extrapolated NT lengths are close to the fitted size of the ANPs

Preliminary Proposal for Composition Effects on Al-Ge-Si Nanotube Length

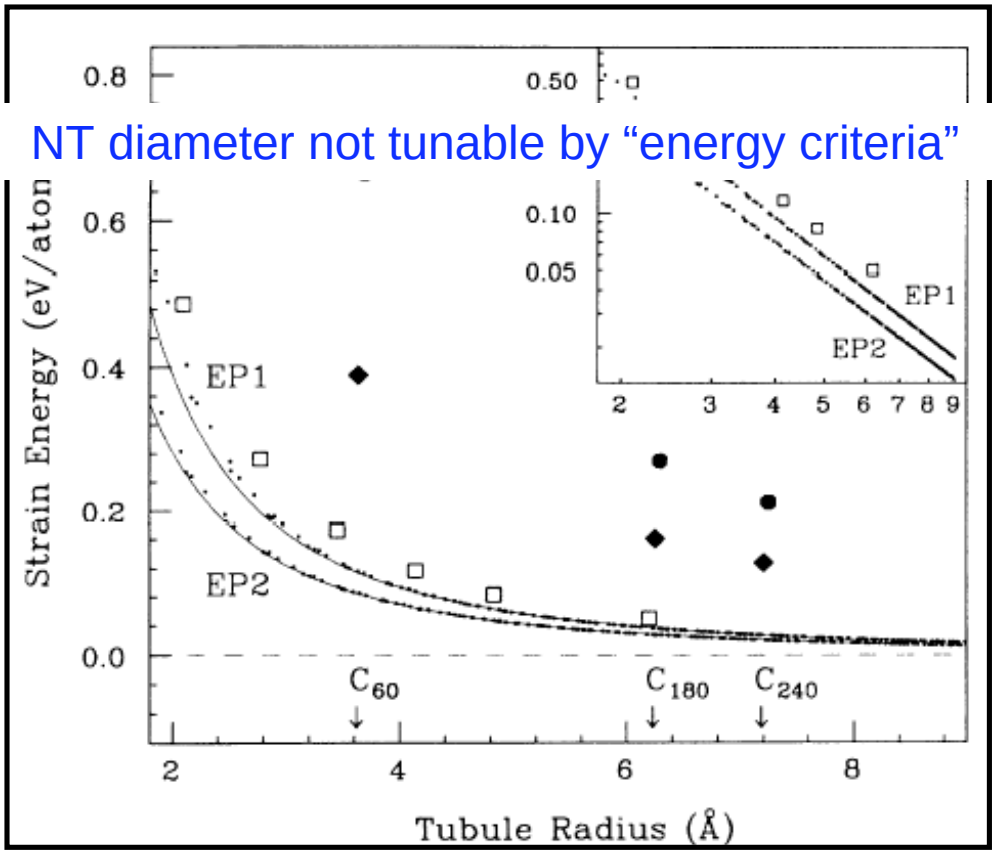
- Analysis within the framework of our ANP → NT mechanistic model
  - Model is supported by detailed studies on Al-Ge nanotubes
  - Tracking of average nanoparticle size by DLS as a function of time and temperature
  - Extraction of NT and ANP sizes using appropriate models of nanoparticle diffusion (rigid rods and spheres)

- Extension of DLS methods to Al-Si-Ge nanotubes
  - ANP diameter and resulting NT length follow the same trends
  - Evidence for strong correlation between these nanoparticle sizes

- Preliminary proposal: As Ge content decreases, the initial condensation process generates larger ANPs which hence transform to larger NTs

- This ‘first order’ model is being developed in more detail – DOSY NMR spectroscopy, optical (IR/Raman/UV-Vis) spectroscopy

Energetics of Carbon Nanotubes



NT diameter not tunable by "energy criteria"

Robertson, et.al. *PRB,* 1992, 45, 12592-12595

- Graphite is the most stable carbon sp^2 structure

  No energy minimum with diameter → polydispersity in NT diameter

Is there a quantitative correlation between the composition, diameter, and internal energy of mixed-oxide aluminosilicogermanate NTs ?

Methodology for Internal Energy Computations

Force field Parameterization

$$E = \frac{e^2}{4\pi\varepsilon_o}\sum_{i\neq j}\frac{q_i q_j}{r_{ij}} + \sum_{i\neq j}\varepsilon_{ij}\left[\left(\frac{R_{o,ij}}{ri_j}\right)^{12} - 2\left(\frac{R_{o,ij}}{r_{ij}}\right)^{6}\right] + k_{ij}(r_{ij} - r_o)^2$$

Optimized Lennard-Jones parameters for Ge using $Na\{AlGeO_4\}$, $K\{AlGeO_4\}$, α-GeO_2 crystal structures

↓

Force field validation *via* structural and vibrational data

↓

Initial NT model construction with varying Si/Ge composition

- NT models constructed as isolated entities to avoid inter-tube interactions
- 3 D periodic boundary conditions

↓

Model structure optimization by energy minimization

Steepest Descent, Conjugate Gradient methods

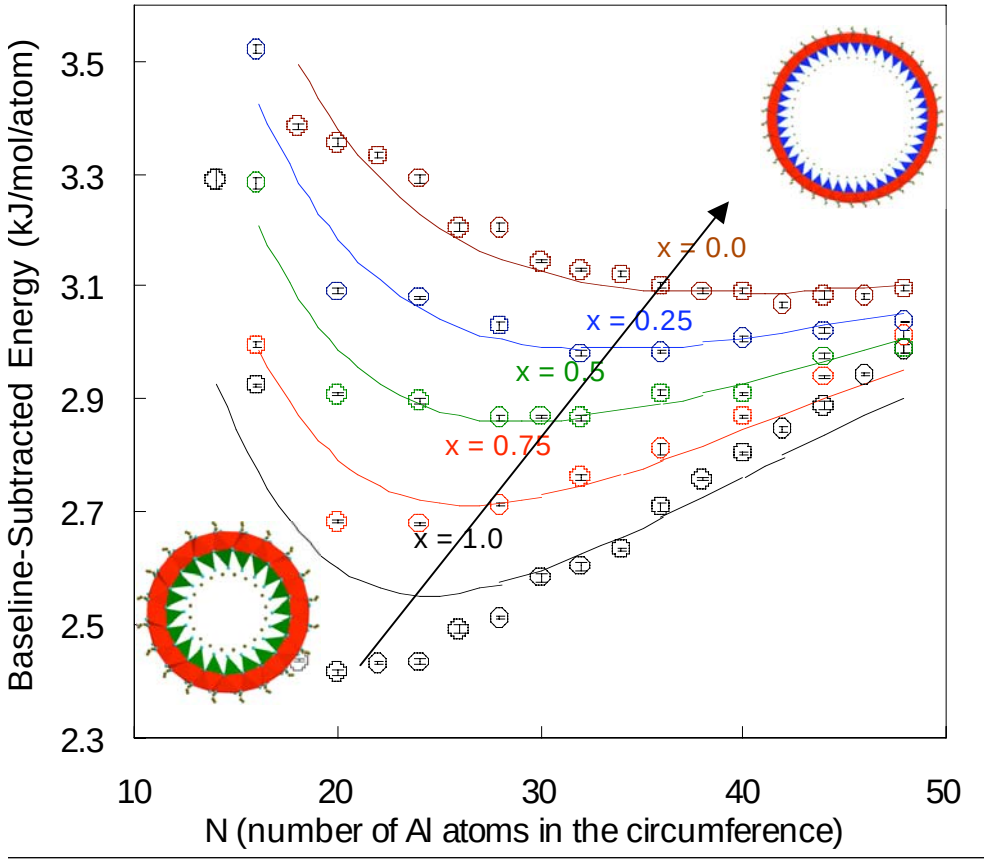
↓

Energy equilibration and data production MD simulations

- NVT@ 298 K using CLAYFF force field*
- Simulation time step used - 0.9 fs
- Berendsen thermostat

Konduri et al, *Physical Review B* (2006)

Total Internal Energy of NTs as a Function of Diameter



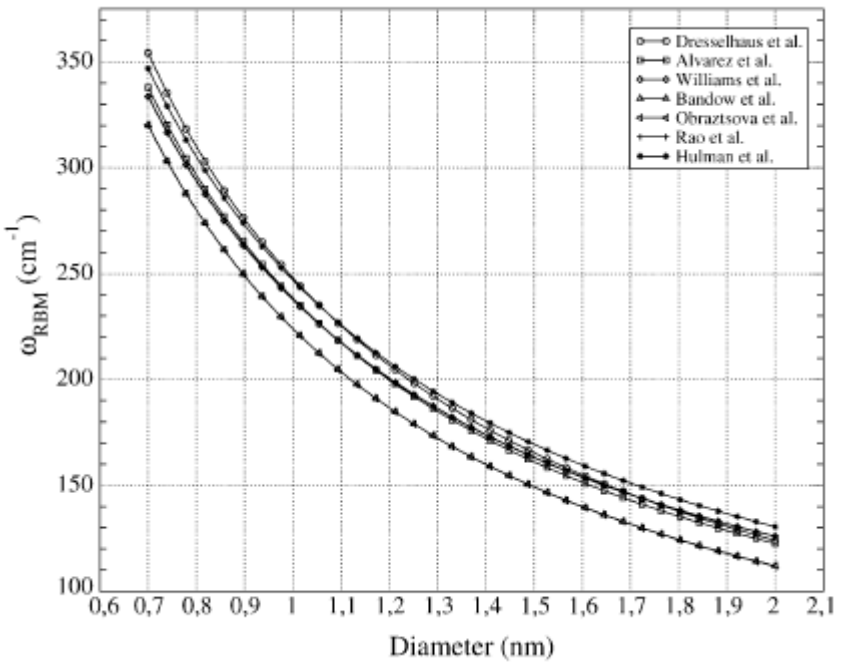
Energy minimum → monodispersity in SWNT diameter

- Energy minima shift progressively to higher diameters with increasing Ge content

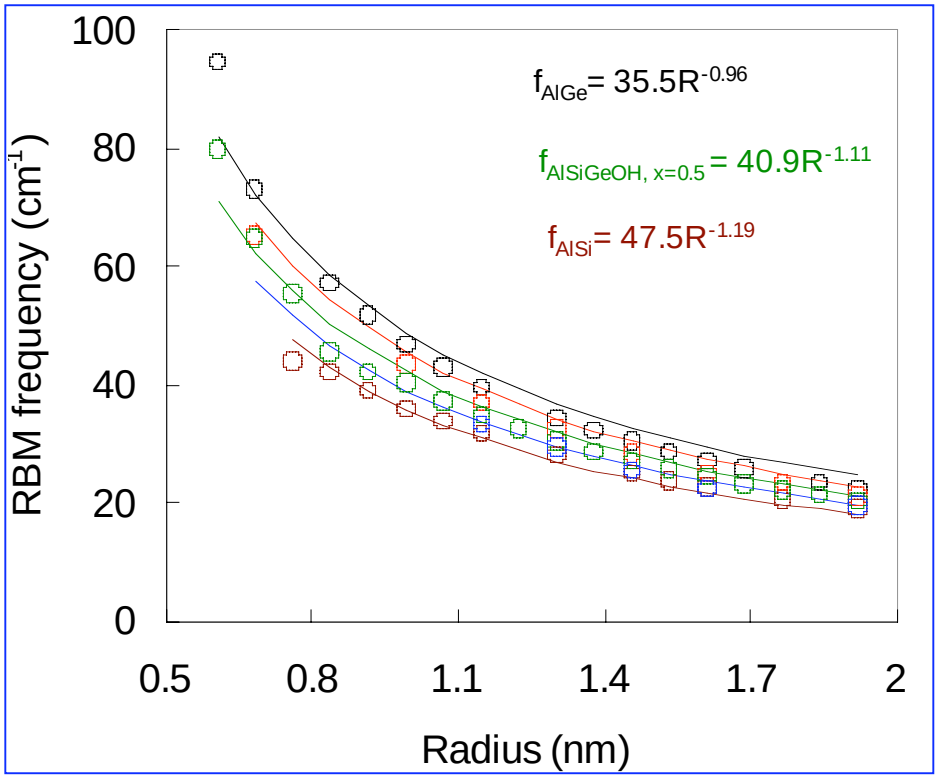
Konduri et al, *ACS Nano* (2007)

Radial Breathing Mode of Single–Walled NT

RBM of CNT



Dresselhaus et al, *Annu. Rev. Mater. Res.* 2004

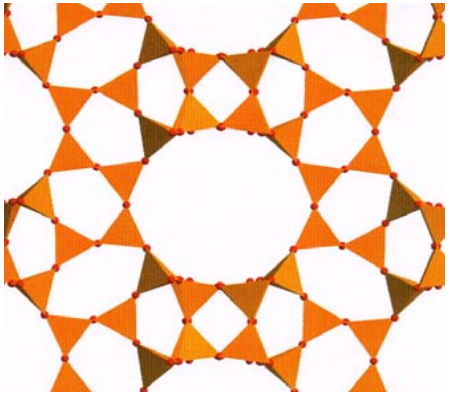


Simulated RBM of AlSiGeOH NTs

- Radial breathing mode (RBM) frequency sensitive to NT diameter
  - Obeys inverse power law dependence on the radius
  - Pre-exponential constant decreases with increase in Ge content -consistent with vibrational frequency shifts in IR

‘Force-Constant’ Model of Nanotube Energetics

- Strain energy model to predict diameters of NT materials
  - E.g. Si substituted by Ge → AlGe NT or varying Si/Ge molar ratios → AlSiGeOH NT



Framework Oxides (e.g., Zeolites)

- 3-D Structures
- Can be modeled as totally ‘rigid’ SiO_4 units with flexible joints
- More than 200 different zeolite structures result from the “flat” energy landscape

Al-Ge-Si Nanotubes

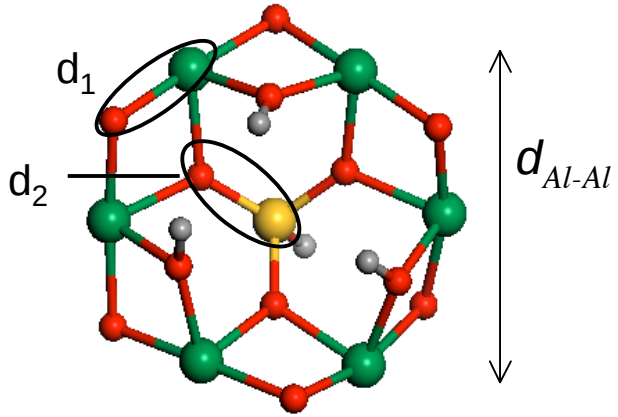
- AlO_6 and SiO_4 are confined into a cylindrical geometry
- Changes in diameter must be accompanied by changes in Al-O and Si-O bond lengths
- Nanoscale confinement effects are important

Hammonds et al, *Phys. Rev. Lett.* 1997, 78, 3701-3704

Force-Constant Model of Nanotube Energetics

- Harmonic potentials to model the Al-O, Si-O, and Ge-O bond energies

$V_{Al\text{-}O} = K_1 (d_1 - d_{1e})^2$, $V_{Si\text{-}O} = K_2 (d_2 - d_{2e})^2$ and $V_{Ge\text{-}O} = K_3 (d_3 - d_{3e})^2$



- Geometric relationships between the bond lengths and the number of Al atoms in the circumference

$$d_{Al-Al} = d_1\sqrt{6}$$

$$d_1 = (2R/\sqrt{6})\sin(2\pi/N)$$

$$d_2 \text{ or } d_3 = d_1/\sqrt{2}$$

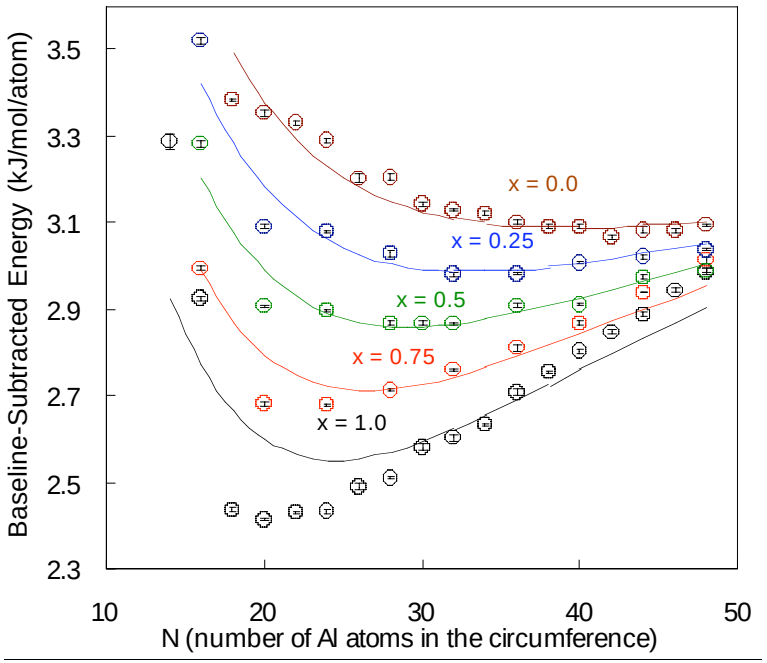
Major axis of hexagon **Al-O bond length** **Si-O/Ge-O bond length**

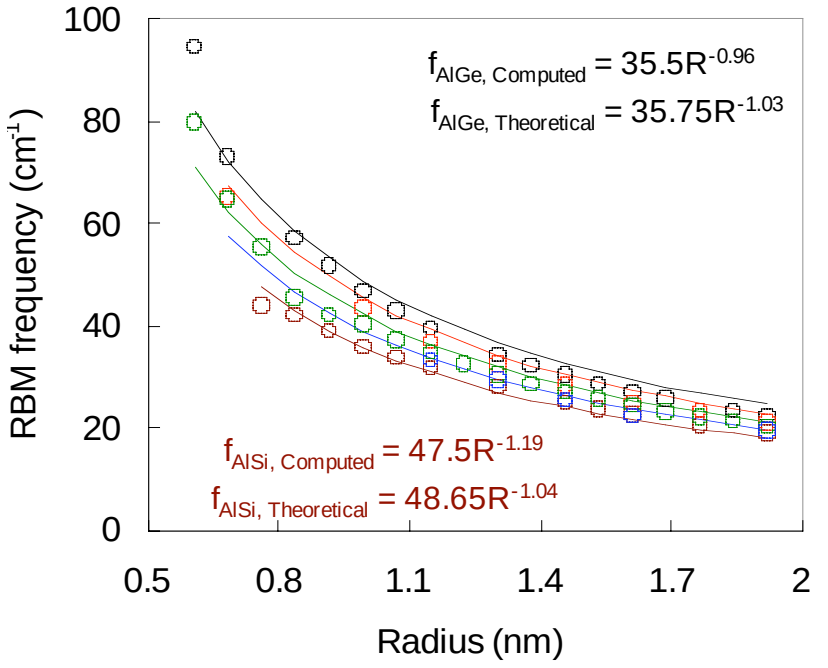
Model Predictions and Fit to Simulation Data

Internal Energy $\overline{E}(N) = \overline{E}_0 + \frac{2}{7}K_1(d_1 - d_{1e})^2 + \frac{3}{14}[xK_2(d_2 - d_{2e})^2 + (1-x)K_3(d_3 - d_{3e})^2]$

RBM frequency $\omega_{RBM} = 2\pi f_{RBM} = \sqrt{4N(4K_1 + 1.5[xK_2 + (1-x)K_3)/3M}.\sin(2\pi/N)$

- Fit results:
  - d_{1e}= 0.197 nm, d_{2e}=0.159 nm, d_{3e}=0.173 nm
  - Strain energy and RBM frequency well reproduced by the model !

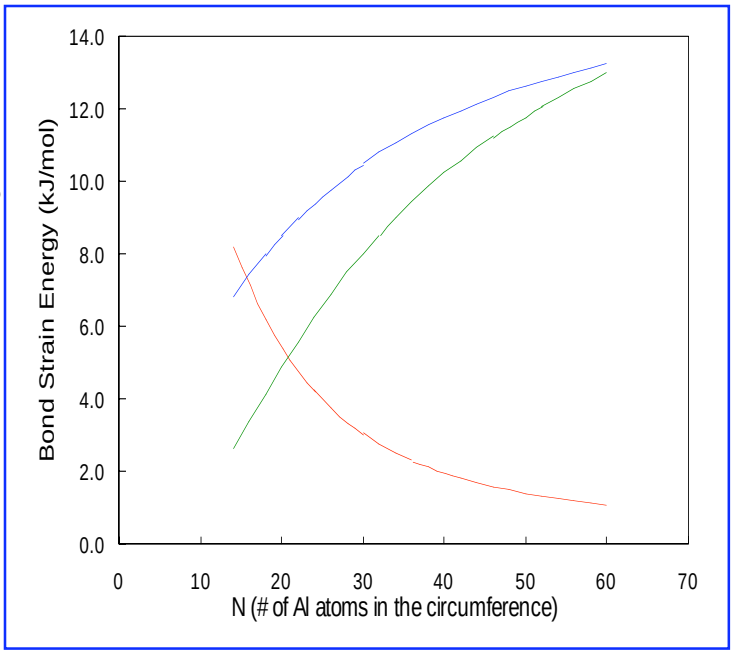




Correlation between NT Composition, Diameter and Internal Energy

- Difference in Si-O/Ge-O and Al-O bond energies induces a strain energy minimum

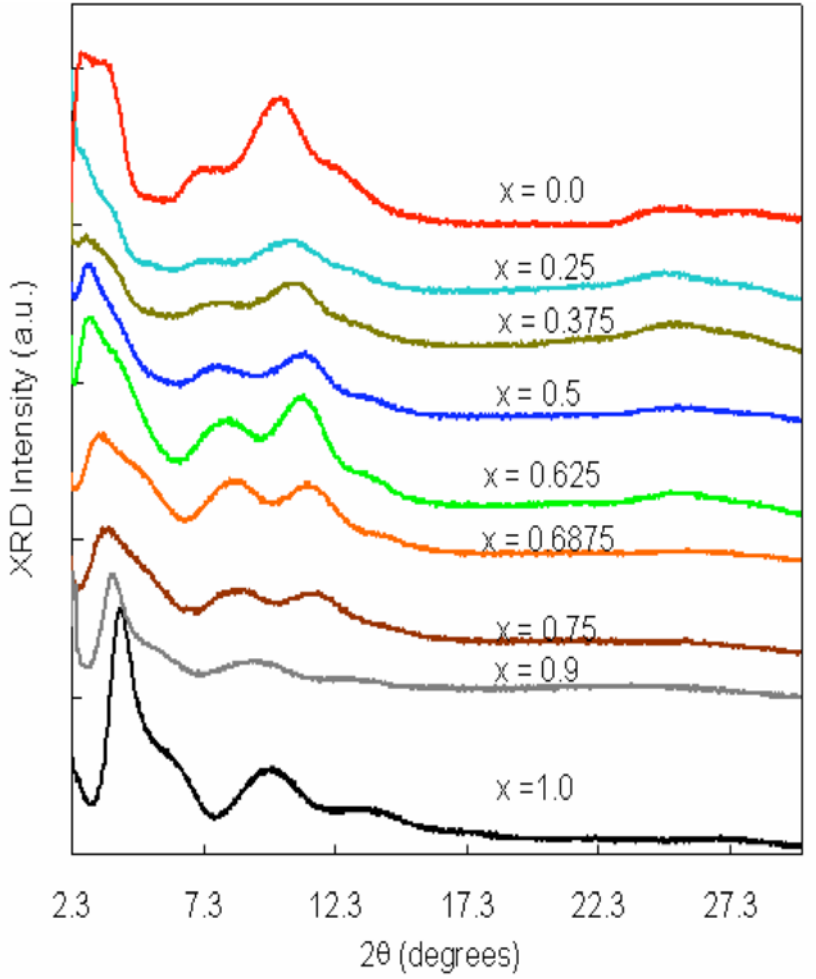
silanols/Germanols



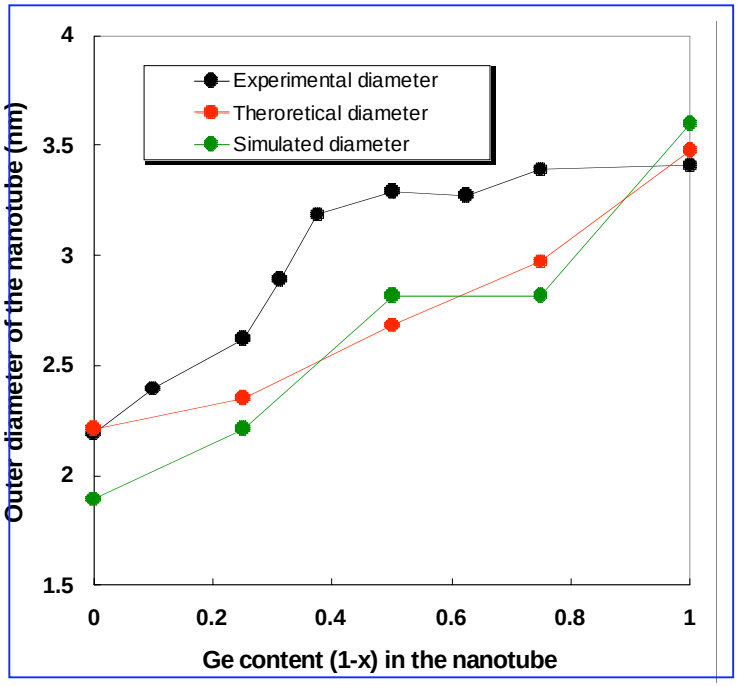
- Ge-O strain potential energy is higher than Si-O
  - energy minimum in AlGeOH NT occurs at larger diameter

- Experimental estimation of the NT diameter
- Quantitative correlation between predicted shift in outer NT diameters and composition estimated *via* XRD
  - First intense peak shifts towards lower 2θ regions with increase in Ge content
  - Indicates that inter-nanotube spacing is increasing

Comparison of Experimental and Predicted NT Diameters



Nanotube diameters from XRD data



- Experimental trends are correctly predicted
  - Quantitative deviations partly due to semi-quantitative relation between XRD peak location and NT diameter

Konduri et al, *ACS Nano* (2007)

Summary

- **Al-Ge-Si-OH single-walled nanotubes: unique nanoscopic objects !**
- **Growth mechanism is quite different from the "nucleation-growth" paradigm existing for nanotube materials**
- **An "amorphous condensation + internal rearrangement" mechanism**
- **There are significant effects of composition on the dimensions (length and diameter)**
- **Nanotube length can be influenced by controlling the amount of material condensed in the amorphous nanoparticles (ANPs), which in turn can be controlled by varying the Si/Ge ratio**
- **Diameter appears to be controlled by internal energy considerations – the existence of a unique energy minimum in the nanotube diameter has been established**
- **Insights to develop synthesis routes based on "amorphous condensation + self assembly" for ordered metal oxide nanoscopic objects of very small dimensions and complex internal structures**